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REGULARITIES OBSERVED IN MIXTURES OF LIQUID
FUEL DURING IGNITION

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REGULARITIES OBSERVED IN MIXTURES OF LIQUID FUEL DURING IGNITION

V. I. Blinov

1. The ignition temperature of a liquid is the lowest temperature for this liquid at which the emergent flame will not be extinguished.

We showed [1] that in the case of the ignition of individual liquids in a cylindrical tube

$$p = p_0(1 - e^{-bh}), \quad (1)$$

where p is the saturated-vapor pressure at ignition temperature; p_0 is the atmospheric pressure; h is the distance of the surface of the liquid from the edge of the tube;

$b = 7.5 \cdot 10^4 M_0 R / p_0^2 D_0 T_1$; D_0 is the diffusivity of vapor at 0°C ; T_1 is the ignition temperature in $^\circ\text{K}$; β is the number of moles of oxygen required for the combustion of one mole of vapor; M_0 is the number of moles of oxygen entering the flame in 1 sec; R is the universal gas constant.

P. G. Ipatov showed [2] that relation (1) holds true for binary mixtures of liquids if we put

$$D_0 = D_{10} y_1 + D_{20} y_2; \quad \beta = \beta_1 y_1 + \beta_2 y_2, \quad (2)$$

where y_1 and y_2 are the mole fractions in the vapor phase of the mixture components.

P. G. Ipatov found the empirical dependences of the ignition temperature on the composition of ideal and nonideal binary mixtures of liquid, but did not explain

these dependences. In this paper, we attempt to explain the basic regularities in the variation of the ignition temperature with variation in the composition of mixtures of liquid fuels.

2. It follows from (1) that the ignition temperature of a specific liquid and of mixtures of liquids is equal to the temperature at which the saturated vapor pressure p is equal to $1 - \exp(-bh)$.

Since the value of M_0 may be considered the same for various materials, given an invariable radius of the tube and an invariable concentration of oxygen in the atmosphere, when $p_0 = \text{const}$ for mixtures of liquids, the ignition temperatures of which do not greatly differ, we may assume that

$$b_0 = 7.5 \cdot 10^4 M_0 R / p_0 T_1 = \text{const.}$$

then

$$b = b_0 / D_0 \beta. \quad (3)$$

If $D_0 \beta$ changes slightly with a change in the composition of the mixtures, then at the given value of h for a mixture of the given two components $p \approx \text{const}$. In this case the dependence of the ignition temperature $\theta_1(^{\circ}\text{C})$ on the composition of the liquid and the vapor phase is graphically represented by curves which coincide with the curves which give the relation between the boiling temperature θ_b and the composition of the phases at constant pressure, determined by relation (1).

It is clear that the curves of $\theta_1(x)$ and $\theta_1(y)$ * when h is variable will differ from $\theta_b(x)$ and $\theta_b(y)$ at constant pressure, but the character of the curves θ_1 and θ_b will be the same. Thus, in the case of nonideal mixtures, with a maximum on the pressure curve there should be a minimum on curves $\theta_1(x)$ and $\theta_1(y)$, while the ignition temperature of the mixtures is lower than the ignition temperature of the mixture components. These curves were obtained by P. G. Ipatov in a study of the

* x and y are the mole fractions of a component in solution and in the vapor phase.

following mixtures: ethanol + benzene (see Fig. 1), ethanol + toluene, methanol + benzene.

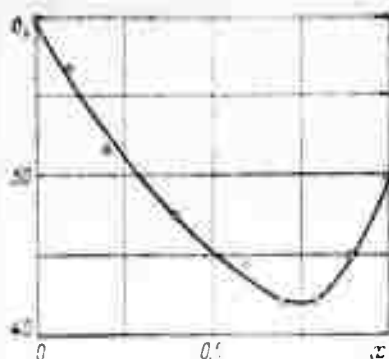


Fig. 1. The dependence of the ignition temperature on the composition of mixtures of ethanol and benzene.

For mixtures with a minimum on the pressure curves, the dependence of θ_1 on x and y should be represented by curves with maxima. The addition of one component to another in this case should lead to the formation of mixtures, the ignition temperatures of which are higher than θ_1 of the pure components. The minima and maxima on the ignition curves should correspond to the azeotropic measures.

In those cases where the mixtures are ideal or close to ideal, the dependences $\theta_1(x)$ and $\theta_1(y)$ should be represented by monotonic curves close to the corresponding boiling curves, which is also confirmed in the work of Ipatov [2].

In the work of Ipatov [2] it was found that for ideal mixtures of toluene and benzene, $\theta_1(y)$ is represented by a straight line. This is easy to explain in the following way. For ideal mixtures

$$p = p_{10} + (p_{20} - p_{10})x_2, \quad x_2 = \frac{a' y_2}{1 + (a' - 1)y_2}, \quad a' = \frac{p_{10}}{p_{20}}. \quad (4)$$

where p_{10} and p_{20} are the saturated vapor pressures of the pure components at the ignition temperature of the mixture; x_2 and y_2 are the mole fractions of the second component in the solution and in the vapor phase.

If the value of p for the given mixtures changes only slightly when x_2 changes and if p is constant, the pressure p will be constant for all practical purposes; let us designate this value of p as p' . Then from (4) we find that

$$a' p_{20} = p' [1 + (a' - 1)y_2]. \quad (5)$$

Let us now designate the ignition temperatures of the mixture and of the second component as T_m and T_2 measured in $^{\circ}\text{K}$. Let $T_m - T_2 = \Theta$ and $\Theta/T_2 \ll 1$. Now we may assume that

$$\frac{1}{T_m} = \frac{1}{T_2 \left(1 + \frac{\Theta}{T_2}\right)} = \frac{1}{T_2} \left(1 - \frac{\Theta}{T_2}\right).$$

Since the saturated vapor pressure is determined by the relation $p = a e^{-\frac{Q}{RT}}$, where Q is the molar heat of vaporization

$$\begin{aligned} p_{20} &= a \exp\left(-\frac{Q}{RT_m}\right) = a \exp\left[-\frac{Q}{RT_2} + \frac{Q}{RT_2^2} \Theta\right] = \\ &= p_{20}' \exp\left(\frac{Q}{RT_2^2} \Theta\right) \approx p_{20}' \left(1 + \frac{Q}{RT_2^2} \Theta\right), \end{aligned} \quad (6)$$

where p_{20} is the saturated vapor pressure of the second component of the mixture at ignition temperature T_2 .

Since the value of α' changes slightly with temperature, it follows from (5) and (6) that

$$\Theta = T_m - T_2 = \vartheta_m - \vartheta_2 = a_1 + a_2 y_2,$$

where a_1 and a_2 are constant; ϑ_m and ϑ_2 are the ignition temperatures of the mixture and the second component.

Taking into consideration the fact that $\vartheta_0 = \vartheta_2$ when $y_2 = 1$ and $\vartheta_0 = \vartheta_1$ (ϑ_1 is the ignition temperature of the first component), when $y_2 = 0$, we will have

$$\vartheta_m = \vartheta_1 - (\vartheta_1 - \vartheta_2) y_2. \quad (7)$$

Relation (7) agrees with the empirical formula found by P. G. Ipatov.

3. The lowest temperature of a liquid at which its vapor forms with air a mixture which ignites in the presence of an ignition source is called the flash-point of a liquid.

The flash-point ϑ_{f1} is closely related to the low concentration limit of the ignition of a mixture of vapor and air. This relation may be determined in the following way. The ignition limit

$$k = \frac{V_v}{V_v + V_a} \cdot 100 = \frac{p_v}{p_v + p_a} \cdot 100,$$

where V_v and V_a are the volumes and p_v and p_a are the partial pressures of vapor and air in a mixture. Since $p_v + p_a = p_0$, when $p_0 = 760$ mm

$$p = 7,6 \text{ k.} \quad (8)$$

Evidently, in formula (8) p equals the saturated vapor pressure at the flash point.

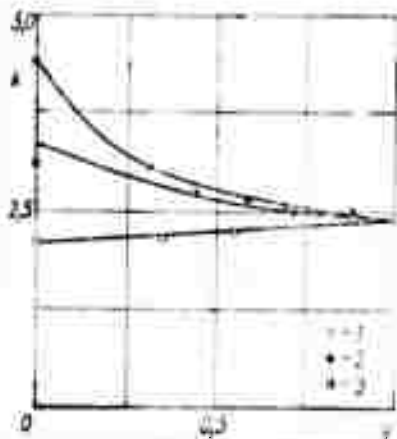


Fig. 2. Dependence of the ignition limit on the composition of the mixtures: 1, 2, and 3 are the results of tests [3] for mixtures, respectively, of benzene with toluene, ethanol with benzene, and acetone with benzene. The solid lines were calculated from formula (10). The value of $\frac{1}{D}$ is taken as the same for all mixtures; the value D was calculated from formula (2). y are the mole fractions of benzene in the vapor phase.

Since the flash point is

close to the ignition temperature, we may use the above relations for the determination of the limit of k . From (1) and (3) when $\frac{1}{D}$ is constant and the value of $\frac{1}{D}$ is small

$$p = p_0 \frac{1}{D} = A/D_0^2. \quad (9)$$

Bearing in mind the fact that the values of $\frac{1}{D}$ in relations (8) and (9) are similar, we may write

$$k = B/D_0^2, \quad B = \text{const.} \quad (10)$$

It can be seen from Fig. 2 that formula (10) satisfactorily describes the given data.

In conclusion, it should be noted that the ignition limit of mixtures is frequently determined by the Le Châtelier principle. This principle, which is an application of the displacement principle to mixtures of liquid fuels, gives results close to those of the tests in a number of cases. If we use it, we would need six empirical constants for the given data in Fig. 2, while when we use relation (10) we need only one constant determined from experiment.

FIRST LINE OF TEXT
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